CONVERTING NATURAL AND METHANE GASES DIRECTLY INTO LIQUIDS

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INTRODUCTION

The recent increase in Crude 0il, gasoline and natural gas prices, dried-up reserves and the petroleum industry's reluctance in increasing petroleum production and drilling any new wells have brought ECONOMICS back as a major player in the development of synthetic (alternate) fuels.

Petroleum experts state that there are approximately 30 to 40 years of crude oil and natural gas left, after all of the enhanced recovery technologies have been utilized. There are about 200 years of coal left. This time line can be increased if we drill into and remove the coalbed methane gas instead of mining the coal.

DOE's Clean Coals Technology Programs has spent \$7 Billion to date for joint venture industry/government investment in a new generation of clean coal technology. Plus millions of dollars have gone into DOE's programs for improving the technologies for coal liquefaction and gas conversion. Some of the programs included revising and modifying versions of the classical Fisher-Tropsch process developed just prior to Word War II and used by the Germans to provide Synthetic Diesel fuel for their Panzer Tanks..

Sasol Ltd. of South Africa and Haldor Topsoe AS of Lyngby, Denmark, have signed a technology cooperation agreement to promote Sasol's Slurry Phase Distillate technology together with Topsoe's natural gas conversion technology for the production of high quality diesel fuels from natural gas.

It is anticipated that this combination will allow the economic conversion of natural gas from any viable source world-wide to high quality environmentally friendly diesel fuels, with the additional potential to produce petrochemicals.

U.S. DOE's Pittsburgh Energy Technology Center's (PETC) let a contract with the Bechtel Group for a Baseline Design/Economics using Advanced Fisher-Tropsch Technology. The plant design includes all process equipment necessary to convert coal to gas and gas to the desired transportation fuels (i.e., gasoline and diesel fuel). In addition, Bechtel has developed an aspen process simulation model to perform additional process sensitivity studies in the future.

DOE/PETC has also issued an amendment to the above study that includes modifying the design model and that the modifications should include the development of an enhanced computer model that incorporates coalbed methane and natural gas feedstocks.

A Synfuels plant provides owners of Coalbeds producing methane Gas.(40% of the gas produced in Alabama that goes into the Interstate Gas Pipeline is Coalbed Methane Gas) plus natural gas reserves, City and County Landfills, Sewer Treatment plants with Digestors and any thing that can produce methane gas, provides an opportunity to capitalize on previously unprofitable resources

As stated in the abstract t'The development of synthetic (alternate) fuels was motivated by the 1990 Clean Air Act Amendment.

The mission for Synfuels is from the Office of Mobile sources, Motor vehicles and Urban buses (extracts from Pages 4 and 5)..

1994 - Truck and buses must meet stringent diesel particulate emission standards, equivalent to 5% of the uncontrolled level. All buses in service in cities with populations of 750,000 or more, to be operated on clean alternate fuels.

1996 - Establishes a new program, initially in California and required in 1996, to require the sale of 150,000 ultra-clean vehicles in the state, increasing in 1999 to 300,000 annually.

<u>Clean Fuels, An Overview, What are Clean Fuels?</u>, The most familiar transportation fuels in this county are gasoline and diesel fuel, but any number of energy sources are capable of powering motor vehicles. These include grain, wood and coal alcohol, electricity, natural and methane gases (including coalbed methane) and propane. Some vehicle fuels because of physical or chemical properties, create less pollution than do to days gasoline. <u>These are called "clean fuels"</u>.

Synthetic diesel fuels derived from methane gas emits, at a minimum, 18% less particulate, 15% less hydrocarbons, and 14% less carbon monoxide than No. 2 diesel fuel. Environmentally friendly synthetic fuels, lubricants and waxes. Synthetic diesel fuel are the cleanest fuel available, and unlike other alternate fuels, does not require any special equipment or engine alterations.

A number of process technologies that convert coal-derived syngas into liquid fuels have been demonstrated at DOE's Alternate Fuels Development Unit (AFDU), located in LaPorte, Texas. U.S. DOE's Pittsburgh Energy Technology Center's (PETC) is presently managing a number of programs for improving the technologies for coal liquefaction and gas conversion.

Gas-to-Liquids Conversion Technologies

Coupling of two methane molecules to higher hydrocarbons is not thermodynamically feasible because the energy of formation is not favorable. However, in the presence of a co-reactant, such as oxygen, the reaction path can be altered, and methane conversion reactions can be successfully camied out. Natural gas (primarily methane) can be upgraded to higher hydrocarbons either by direct conversion routes (single-step or staged), or via synthesis gas (a mixture of carbon monoxide and hydrogen). The important process considerations for commercially viable natural gas upgrading operations are methane conversion rate and selectivity to preferred products.

Based on chemistry, the processes for natural gas upgrading include 1) partial oxidation to oxygenates, such as methanol, 2) oxidative coupling to higher hydrocarbons, such as ethylene, 3) derivatization, such as oxyhydrorochlorination to chlorinated hydrocarbons, which are subsequently converted to higher hydrocarbons, and 4) pyrolysis to aromatic and/or higher hydrocarbons.

In the indirect process, natural gas is first converted to synthesis gas, followed by catalytic hydrocarbon of the carbon monoxide in a synthesis reactor to a variety of higher hydrocarbon fuels. Fisher-Tropsch (FT) synthesis and its variants are important synthesis reactions, involving low-pressure conversion of synthesis gas to gasoline, diesel fuel, wax, and oxygenates. The products of reaction depend on the temperature, pressure, and catalyst used in the synthesis reactor.

PETC's Gas-To-Liquids Program

The goals of PETC's Gas-To-Liquids Program can be summarized as follows:

- Discover new chemistry and catalysts for the conversion of methane and other light hydrocarbon gases to value-added, easily transportable fuels and chemicals
- Obtain necessary design and engineering information to develop prototype technologies for demonstration and commercial deployment.
- Pursue cost-shared, risk-shared, industry-driven R&D, demonstration, and technology transfer to ensure pay-off of Federal R&D investments.

- Contribute to energy policy goals by selecting investments consistent with the four major policy thrusts:
 - Energy security
 - · Economic growth
 - Environmental quality improvement
 - Enhancing scientific foundations.

Some of the Synfuel development milestones:

I DOE Contract No. DE-AC-911PC90027 with the Bechtel Group, This Advanced Fisher-Tropsch indirect Liquefaction Study is for the conversion of Coal to gas and the gas into liquids:

The present indirect liquefaction technology is the base for Bechtel's baseline design study, the PFS model, developed for a wide range of plant capabilities and operating parameters, is a research tool for evaluation of future technology advances. This effort was a logical continuation of Bechtel's baseline design study and will provide additional capabilities to the model for future use with the appropriate modifications of the current baseline design and computer mode, any hydrocarbon feedstock can be used.

2 PETC has amended Bechtel Group's contract for the modification of Bechtel's baseline design study to include an economic analysis for <u>natural gas and coalbed</u> <u>methane gas as feedstock.</u>

Capital and operating costs are called for in the contract, this will also include individual plant costs for the alternative cases.

An ASPEN/SP Process Flowsheet (PFS) model and an economic spreadsheet model. Sensitivity studies have been performed to demonstrate the effects of key independent process variables and economic assumptions.

Some Synfuel Plants in Operation

A 14,500 BPD natural gas-to-gasoline plant started operating in New Zealand in 1985 and is on stream producing 87 octane unleaded gasoline. In this process, natural gas was first converted to methanol via synthesis gas, followed by conversion of methanol to gasoline using a novel catalyst developed by Mobil in the 1970s.

In April 1993, Exxon announced its AGC-SA Advanced Gas Conversion Technology for converting natural gas to high quality refinery feedstock. Olefin-based transportation fuels from natural gas is produced in the Mossgas plant in South Africa.

The Shell Middle Distillate Synthesis (SMDS) process is by now well known as Shell's development to broaden the basis of natural gas utilization.

This technology is now being applied by Shell MDS (Malaysia) Sendirian Berhad in a first full scale application of 12,500 bbl/day, which was started in Bintylu, Sarawak in 1993. The plant produces automotive fuels of exceptional quality, and , in addition to this, special chemicals and waxes. Flexibility in the process operation allows for a wide range of product selection, which is a valuable asset in a variable market.

Because of these excellent properties, which are in particular far in excess of the market minimum specifications for smoke point and cetane number, these products make excellent blending components for upgrading of lower quality stock derived from conventional crude oil processing or catalyst and thermal cracking operations e.g. cycle oils The linear blending characteristics of Shell MDS gasoil, shows that the addition of some 35 per cent (35%) of SMDS gasoil to a typical naphthionic gasoil is sufficient to raise the cetane number from 33 to the required specification of 47...

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There are other Synfuel Plants, a operating Industrial demonstration plant in Shanxi province, China and a plant by Intevap in Venezuela

Due to the nature of the feedstock, products do not contain any sulfur or nitrogen and conform to the new EPA Clean Air Act regulations with respect to particulate emissions, sulfur and aromic content. Distillates from this process are finding a premium value in the market .

The MITRE Corp., McLean VA, a DOE consultant is analyzing a number of Synfuels plant technologies resulting in lowering plant cost and operating reductions. MITRE Corp. DOE contract is to review the development of any technologies that can reduce the costs in Bechtel's technoeconomic analysis

An extensive report prepared November, 1991 by the MITRE Corp., McLean, VA (under a DOE contract) in the form of a technoeconomic analysis for The Great Plains Synfuels plant in Beulah, North Dakota that is developing a Hybrid Plant Coal Liquefaction Concept for a 2,000 barrel per day Synfuels plant.

The report analyzed a number of liquefaction processes and found that the Rentech, Inc. process is rated one of the best economically. Ref. to Page 50 Figure #8-1 Rentech - 1 Indirect shows 640 BPSD times Incremental Capital = \$6.8 Million.

Incremental Capital costs of \$6.8MM (Million) to produce 640 Total Liquids (BPSD) - Barrels (26,880 gallons) per day. In the Report's Section 8.2 "Economic Evaluations" shows the varies rates of return. What it does not show is the fact that Synfuel plants can eliminate approximately 60% of the front-end cost of using direct coal liquefaction technologies in their design/build process.

Other products produced by a Synthetic Fuels Plant.

Wal Mart is selling a Biodegradable Motor oil for approximately \$3.00 a Quart. (You can buy Regular Motor oil from Auto Zone or Checker for \$.85 to \$1.25 a quart). Wal-Marts supplier is Synthetic Oil Services International (SOS), McLean, VA. SOS also offers a synthetic low smoke biodegradable motor oil formulated for outboard manne use.

WAXES

Waxes produced from Synfuels plants are known as Fisher-Tropsch (F-T) waxes, and have the potential to be refined to compete with F-T waxes currently produced in South Africa. They have a very high molecular weight, melting point, and have excellent hardness. F-T waxes are similar to petroleum hydrocarbon waxes with the exception that they have a higher proportion of higher melting, linear molecules.

The United States alone consumes approximately 25 - 30 million pounds of F-T waxes each year. However, until now, no F-T waxes was produced in the United States. About one-half of the waxes consumed in the U.S. are used in hot melt adhesives, 25 - 30 percent in inks and coatings, mainly as micro pulverized materials, and the balance in a large variety of applications as:

- * Candles
- Crayons
- Lipsticks
- * Textiles
- · Resin-wax polish formulations
- * Paste and emulsion polishes for floor ,furniture and automobiles
- Anticorrosion coatings
- Internal lubricants and mold-release agents for plastics

NAPHTHA

Naphtha produced by the Synfuels process can be used as a feedstock for chemical processing or refined to be used in the following products:

Varnish maker and paints Type IV mineral spirits Petroleum ether Textile spirits and ink oil

While Liquid Hydrogen is the fuel of choice for a space-launch vehicle that accelerates quickly out of the atmosphere, studies have shown that liquid methane is better for an aircraft cruising at Mach 5 to Mach 7.

Methane (either natural gas or coalbed methane gas) is widely available, provides more energy than jet fuels, and can absorb five times as much heat as kerosene. Compared with liquid hydrogen, it is three times denser and easier to handle. This is the fuel used by the U.S. hypersonic spy plane, Aurora SR-71.

CONCLUSIONS:

As seen in table 1, by converting Natural gas or Coalbed methane Gas extracted from the Coalbeds directly into liquids can save a total of 72% compared to Coal liquefaction.

The environmentally friendly products produced from a Synthetic fuels plant, such as biodegradable motor oil, marine oil, lubricating oils can save millions of dollars now being spent in oil clean-up costs of used motor oils and petroleum based lubricants.

As stated earlier, Synfuels plants provides owners of Coalbeds producing methane Gas plus natural gas reserves, City and County Landfills, Sewer Treatment plants with Digestors and any thing that can produce methane gas, provides an opportunity to capitalize on previously unprofitable resources

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Table 1. Element of cost - Bechtel Design costs in a indirect coal liquefaction baseline plant where further reductions in costs may be possible.

	%	OMIT
Coal Handling	6	OMIT
Gasification	32	OMIT
Oxygen Plant	14	OMIT
Byproduct Recovery	3	
Fisher-Tropsch Synthesis	7	
Syngas Recycle Loop	12	
Product Refining	6	
Field Cost	20	OMIT
TOTAL	100	